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Isotopically Enriched ^{28}Si Crystals for Electronics Applications

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PRINCIPAL INVESTIGATOR:
Tso-Ping Ma, Professor

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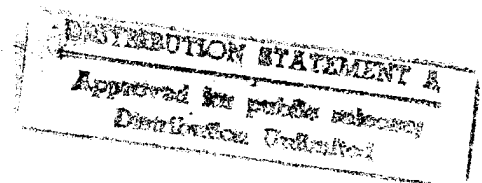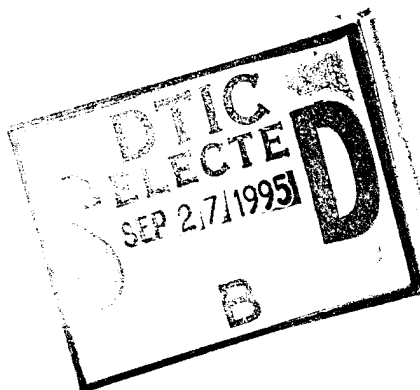
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The Yale Center for Microelectronic Materials and Structures

and

Department of Electrical Engineering

YALE UNIVERSITY

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Isotopically Enriched ^{28}Si For Electronics Applications

Contents

Isotopically Enriched ^{28}Si For Electronics Applications

1 Objective

The objective of this research is to study the thermal and electronic properties of isotopically enriched ^{28}Si epitaxial films which are potentially attractive for high-density, high-speed electronic circuit applications.

2 Theoretical Considerations

The natural abundance of Si is roughly 92.2 % of ^{28}Si, 4.7 % of ^{29}Si, and 3.1 % of ^{30}Si, which is also roughly the composition of Si crystals currently used in industry. By removing the heavier isotopes (i.e., ^{29}Si and ^{30}Si), it is very likely that the enriched ^{28}Si crystal will have a much better thermal conductivity and carrier mobility, due to the reduction of the scattering centers arising from the heavy isotope 'impurities'.

Significant improvement of thermal conductivity in synthetic diamond has recently been demonstrated in isotopically enriched ^{12}C [1,2]. In the case of carbon, the heavier isotope ^{13}C has only $\sim$ 1% concentration in its natural abundance, and yet the GE researchers were able to achieve 50 % higher thermal conductivity in their synthetic diamond by reducing it to a lever of $\sim$ 0.1 % [1,2]. In the case of Si, the total natural abundance of the heavier isotopes (combining both ^{29}Si and ^{30}Si) is approximately 8 %, or 8 times higher than that of ^{13}C. Therefore, it is conceivable that the improvement of thermal conductivity in high purity ^{28}Si could be equally significant.

In fact, significant improvement of thermal conductivity in isotopically enriched ^{74}Ge was reported more than three decades ago [3], and a model existed which explained why one would expect such an isotope effect [4]. While the theory presented in [4] is very rough, it does predict the right trend, and provides encouragement for this proposed research project.

No publications have been found that address the effects of isotopes on carrier mobility, either theoretically or experimentally. However, it seems reasonable to treat the isotope atom as a point scattering center due to its different mass from the majority atoms in the host crystal. In the context of electron (or hole)-isotope scattering, the isotope atoms may be treated as a neutral impurity, in addition to the effect of the perturbed phonons. While the scattering cross sections of the isotopes may be low, their extremely large numbers (of order of 4×10^{21}/cm^3, compared to the typical channel dopant level of $\leq 10^{17}$/cm^3) could still have a significant effect on the carrier

mobility. By similar arguments, the saturation velocity may also be increased.

3   Progress to Date

During the past two years, our research effort was devoted to:

a) growth of epitaxial ^{28}Si films by MBE (in collaboration with Prof. Kang Wang)
b) growth of ^{28}Si mini-crystals (in collaboration with Prof. Bruce Chai)
c) experimental considerations of thermal conductivity measurement
d) design and construction of sample holder and measurement apparatus
e) design and fabrication of test device structures for thermal conductivity measurements
f) preliminary measurements of thermal conductivity in regular Si samples
g) preliminary measurements of ^{28}Si minicrystals

These are are summarized below.

3.1   Growth of Epitaxial ^{28}Si Films by MBE

Although it may be more advantageous to grow the epitaxial ^{28}Si films by the CVD method, that option was dropped because of the unavailability of appropriate precursors containing ^{28}Si. Instead, we decided to use the MBE growth method after we acquired sufficient amount of ^{28}Si powders. Since we do not have Si MBE capability at Yale, we initiated a collaborative effort with Professor Kang L. Wang at UCLA in which he agreed to grow the epitaxial ^{28}Si samples using his MBE machine. So far his student has tried half a dozen growth runs, but because of the severe source outgassing problem, these attempts were not successful. Because of his other commitments, Professor Wang has decided to table this experiment until we can supply him with more suitable ^{28}Si source material.

3.2   Growth of ^{28}Si mini-crystals

We initiated a collaborative effort with Professor Bruce Chai at the University of Central Florida to grow mini-crystals of ^{28}Si using two different methods: (1) Laser Heated Pedestal Growth (LHPG), and (2) Melt-Freeze (MF) technique. After several attempts, Prof. Chai was able to grow silicon fibers out of standard silicon bouls by the LHPG method, but not out of the ^{28}Si source material (in the form of hot-pressed podwer) that we sent him. He also grew large-grain polycrystalline droplets out of the ^{28}Si source material by the MF method.

The key results of these crystal growth experiments have been presented at the

9th American Conference on Crystal Growth held in Baltimore on Aug. 3-6, 1993. A copy of the transparencies presented at the conference is attached as an Appendix.

3.3 Experimental Considerations of Thermal Conductivity Measurement

Based on the assumption that we would have availabe epitaxial ^{28}Si films grown on regular Si substrate, we decided to design appropriate experiments to measure the thermal conductivity of the epi film. Because of practical limitations of Si MBE, the epi layer thickness will be limited ($\leq 2\mu$m). Thus, the major challenge of the measurement is to be able to separate the thermal conductivity contribution of the epi layer from that of the bulk Si substrate. This requires that the thermal conductivity of the epi layer to be much higher than that of the bulk Si substrate. For this reason, the Si substrate would be heavily doped ($\sim 10^{20}$/cm^2), while the epi layer would not be intentionally doped.

The thermal conductivity of the epitaxial films would be measured by the thin film micro heater and sensor technique described in [6,7]. Essentially this technique utilizes a lithographically defined set of closely spaced narrow metal stripes on the sample, with one stripe serving as the heater and the others serving as sensing elements. The heater stripe is excited by a current which lauches a cylindrical heat wave into the sample, that produces a temperature gradient whose magnitude depends on the power applied to the heater, the boundary scattering, and the thermal conductivity of the underlying sample. The detailed theory for this technique has been described in [6,7], and we have written a computer program for analyzing the experimental data.

Another approach that we have considered involves an etch-back technique to remove the substrate material in the region where the thermal conductivity of the ^{28}Si epi-layer is to be measured. Proper masking scheme and selective etching techniques must be first established if the etch-back approach is to be implemented.

3.4 Design and Construction of Sample Holder and Measurement Apparatus

The test chip is bonded on a multipin flat-pak, which is then mounted on a special sample holder. The sample holder, made of a copper block for its good thermal conductivity, is mounted on a cold finger of a cryostat whose temperature can be controlled within 0.02 K in the range 20-450 K. A Keithley 220 current source, a K-199 multichannel voltmeter, and a K-181 nanovoltmeter serve as the heater current supply and sensor voltage measurement, respectively. Preliminary experiments suggest that the apparatus is adequate for the intended application. Automation of the measurements and data acquisition procedure by the use of a PC has been

implemented.

3.5 Design and Fabrication of Test Device Structures

The mask layout consists of 5 narrow metal stripes, with a linewidth of 7 μm and a length of 2mm each, and the spacing between stripes is 13 μm. Four-probe contact pads are provided for each stripe.

Test device structures have been fabricated on high-resistivity ($\sim$5kΩ-cm) Si wafers using Al metallization. A thermal SiO_2 layer, 50 nm thick, serves as an electrical insulator.

Some measurements have been made on these test structures, as described below.

3.6 Preliminary Measurements of Thermal Conductivity on Regular Si Samples

Using the thermal conductivity measurement apparatus described above, we have obtained some preliminary data on high-resistivity regular Si wafers over a temperature range of 20-300 K. In the range 20-50 K, the thermal conductivity monotonically increases with temperature from $\sim$10 W/cm-deg at 20 K to a peak of $\sim$25 W/cm-deg at 50 K; in the range 50-300 K, the thermal conductivity decreases monotonically to $\sim$5 W/cm-deg at 300 K. These data, while not in exact quantitative agreement with those published in the literature, are certainly in the right ball park, and provide encouragement for further refinement.

From our measurements performed so far, we believe that our apparatus is capable of detecting a temperature difference as small as 10^{-3} K between two metal stripes, which should be sufficient for samples with a thermal conductivity as high as 100 W/cm-deg.

3.7 Measurements on Polycrystalline ^{28}Si Droplets

Although we have not been able to grow single-crystal ^{28}Si, we decided to analyze the polycrystalline ^{28}Si which Prof. Chai obtained from the MF method. The van der Pauw 4-point probe measurement indicates an extremely high carrier density ($\sim 6\times10^{19} cm^{-3}$), suggesting a very high concentration of electrically active impurities. Such a high impurity content will mask any isotope effect on the thermal conductivity. Indeed, our thermal conductivity measurement performed in a temperature range between 20K and 300K shows that the data are similar to those published for regular silicon with equivalent impurity concentration. A more detailed description of the results can be found in the Appendix.

4 Concluding Remarks

While the scientific idea of this research project seems straightforward enough, the actual execution has proved to be much more difficult than originally expected, and the desired outcome has so far been elusive.

The major difficulty arose from the lack of sufficient quantity of the ^{28}Si source material to begin with. Because of this deficiency, we were forced to attempt the growth of single-crystal ^{28}Si by whatever means which could accommodate this limitation, rather than having the freedom of choosing the best crystal growth technique. In this context, it may be worth mentioning that a group of U.S. and Russian Researchers recently succeed in growing isotopically enriched ^{70}Ge and ^{74}Ge single crystals with extremely high purity [7]. Such a high purity was made possible by a zone purification process which required 100 g each of the starting ^{70}Ge and ^{74}Ge materials. In contrast, we have only 9 g of ^{28}Si to work with. Although not mentioned in the paper [7], one of the authors told me that they are now doing thermal conductivity measurements on these samples.

Nevertheless, our recent paper at the 9th American Conference on Crystal Growth received some considerable attention. Professor Joseph Milstein at Lowell University, who has worked extensively on magnetic levitation of zone refining Si, indicated that it is possible to remove the impurities in our samples, and would be interested in collaborating with us. We are in the process of discussing this possibility.

In addition, Dr. Carl Sheibner of Lowrence Livermore, whose expertise is in isotope separation by high-power lasers, has also indicated his desire to collaborate, and there is a possibility that large quantities of ^{28}Si may become available through his effort in the future.

Therefore, although this research contract has officially ended, we will continue to work on this project, and hopefully will be able to eventually obtain the results that we predicted.

5 References

1. New York Times article 'GE Sees Breakthroughs from New Diamond', published on page D6 of the July 11, 1990 issue.

2. Anthony et al., 'Thermal Diffusivity of Isotopically Enriched ^{12}C Diamond', Phys. Rev. B, 42, 1104 (1990).

3. Geballe and Hull, 'Isotopic and Other Types of Thermal Resistance in Ge,' Phys. Rev., 110, 773 (1958).

4. Slack, 'Effect of Isotopes on Low Temperature Thermal Conductivity', Phys. Rev., 105, 829 (1957).

5. Collins et al., 'Indirect Energy Gap of ^{13}C Diamond', Phys. Rev. Letters, 65, 891 (1990).

6. Cahill et al., 'Thermal Conductivity of Thin Films: Measurements and Understanding', J. Vac. Sci. Technol. A 7(3), 1259 (1989).

7. Cahill and Pohl, 'Thermal Conductivity of Amorphous Solids above the Plateau', Phys. Rev. B, 35, 4076 (1987).

8. Itoh, et al., 'High Purity Isotopically Enriched ^{70}Ge and ^{74}Ge Single Crystals: Isotope Separation, Growth, and Properties', J. Mater. Res., 8, 1341 (1993).

6 Publications/Presentations

1. B. Chai, R. Jarman, A. Wallenberg, T. Ma, and K. Scheibner, 'Laser Heated Pedestal Growth of ^{28}Si Single Crystals', *9th American Conference on Crystal Growth*, Baltimore, Maryland, Aug. 3-6 (1993).

Appendix

Laser Heated Pedestal Growth of ^{28}Si Single Crystals

B.H.T. Chai
CREOL, University of Central Florida
Orlando, Florida 32826

R.H. Jarman, A.J. Wallenberg
Amoco Technology, Co.,
Naperville, Illinois 60566

T.P. Ma
Dept. of Electric Engineering, Yale University
New Haven, Connecticut 06510

K.F. Scheibner
Lawrence Livermore National Laboratory
Livermore, California 94551

§   Introduction:

◊ In 1990, G.E. researchers T. R. Anthony et al discovered that isotopically pure ^{12}C (Type IIA) diamond has 50% higher thermal conductivity than natural diamond (containing only 1% ^{13}C)

Material	Thermal Conductivity (W/cm°K)
0.07% ^{13}C diamond	33.2
1% ^{13}C natural diamond	22.3
SiC	4.9
Cu	4.0
BeO	3.7
Si	1.6
MgO	0.6
Al_2O_3	0.4
YAG	0.14

◊ For dielectric solid, the thermal conductivity is

$$K = 0.333 \ CV\Lambda$$

where   C = specific heat of phonon assemblage
         V = phonon speed ≈ sound velocity
         Λ = phonon mean free path

◊ For high purity, low defect crystals, the thermal resistance is caused by phonon-phonon and phonon-isotope scattering.

$$1/\Lambda = 1/\Lambda_{ph\text{-}ph} + 1/\Lambda_{isotope}$$

For diamond, $\Lambda_{ph\text{-}ph} \approx 30$ nm and $\Lambda_{isotope} \approx 2600$ nm. The measured isotope effect is significantly bigger.

◊ Natural Si contains 4.67% ^{29}Si and 3.10% ^{30}Si, we expect greater improvement in thermal conductivity for pure ^{28}Si.

◊ By removing isotope as point scattering centers($4 \times 10^{21}/cm^3$ as compared to typical dopant level of $\leq 10^{17}/cm^3$)

§ General Background:

◊ So far, we do not aware any research on isotopically pure silicon single crystals

-- small quantity of materials available
-- no suitable crystal growth method

◊ To accommodate the constraints, we decided that laser heated pedestal growth (LHPG) is the best technique to get the small single crystals for investigation.

◊ Although LHPG method is well established for the growth of oxide and fluoride crystal fibers, there is only one paper describing the growth of Si fiber.

-- This is because Si is too transparent to 10.6 μm CO_2 laser

-- The absorption in oxides is primarily by phonons whereas the absorption in silicon is by free carriers.

◊ Kim at al at RCA Laboratory (J. Appl. Phys. 50, 4472 (1979) successfully produced silicon fibers 0.25 to 0.70 mm. They estimated the power required for 1 mm dismeter silicon is 100W !!!
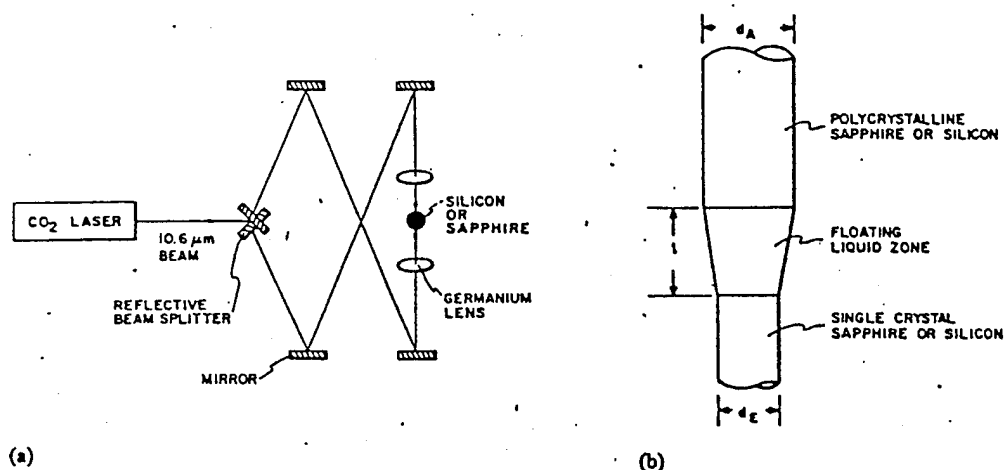

FIG. 1. A schematic representation of the crystal-growth arrangement using CO_2 laser: (a) the laser optics and (b) floating zone.

(a)   (b)

§ LHPG of ^{28}Si Crystals:

◊   Single crystal silicon fiber growth is carried out at Amoco Technology, Co. where a State-of-the-art high vacuum (10^{-6} torr) LHPG system is located.

◊   Starting materials

--   Standard silicon boules cut to both (100) and (111) oriented rods were used for test runs
        -- both seed and feed stock (0.5 and 1 mm dia.)

-- ^{28}Si rods (1 mm dia.) cut from a sintered disk (from Russia)

-- ^{28}Si powders (1.98 gms) from Oak Ridge National Lab.
        --   not suitable for this work

◊   We are under powered

        --   The maximum power of our CO_2 laser is 50 W
        --   We managed to deliver 43 W focused beam to target
        --   The power can not sustain large diameter rods

Layout of major components for LHPG. Pieces are as follows:

a. Edinburgh PL5 CO_2 laser
b. Lasnix attenuator
c. Klinger polarization attenuator
d. beam dump
e. HeNe laser
f. beam combiner
g. II-VI beam-expanding telescope
h. Periscope
i. Growth chamber
j. Long distance microscope
k. CIDTEC cameras
l. x-y-z stages
m. Operator viewport
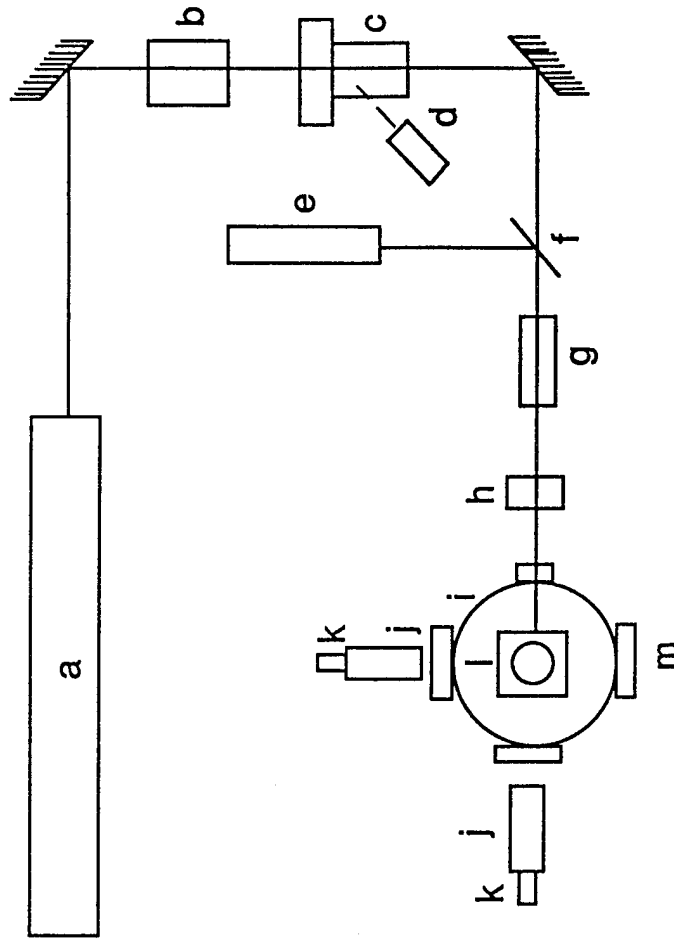
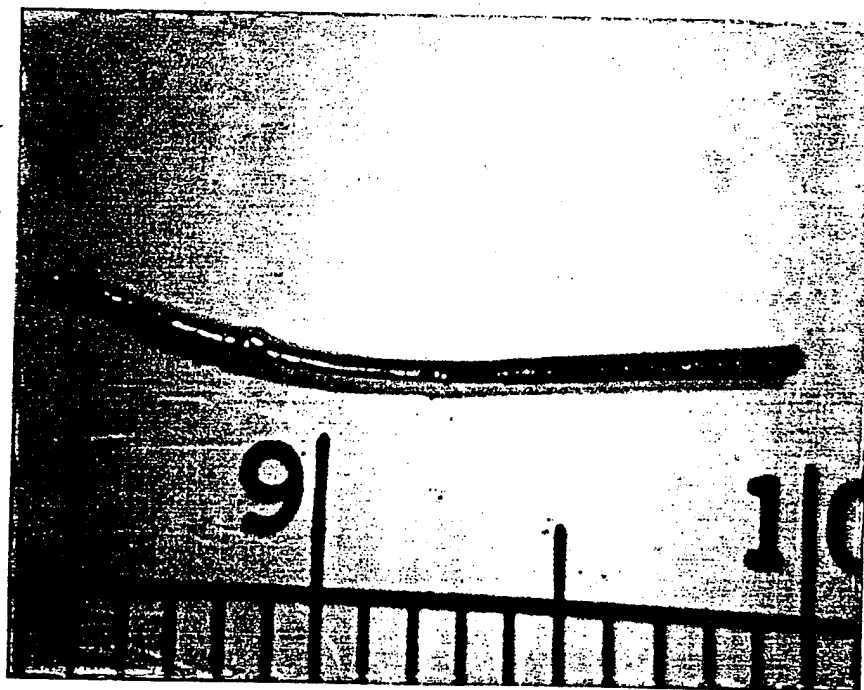## § Experimental Result (Regular Silicon):

◊ Despite the severe power limit, we managed to grow regular silicon single crystal fiber of 0.3 mm in diameter for both (100) and (111) directions.
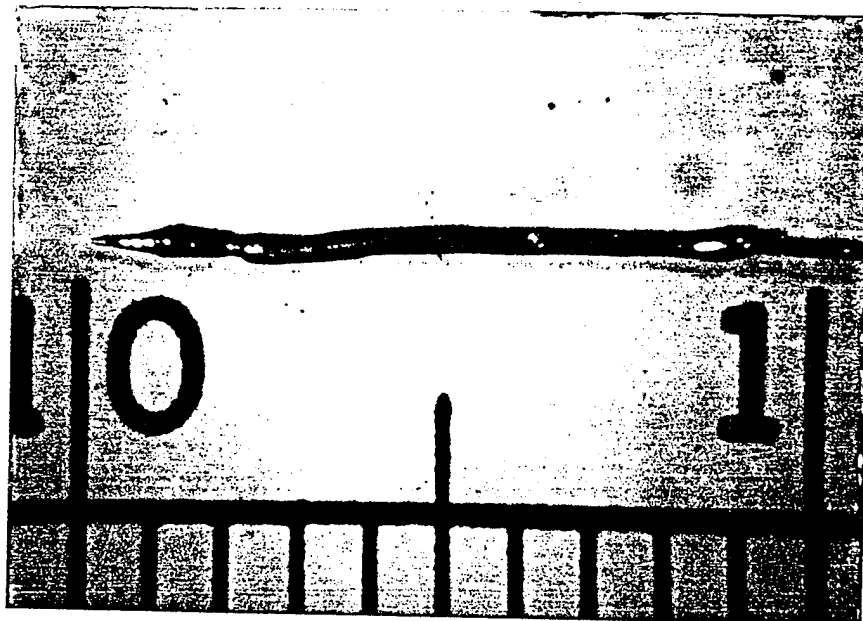
§ Experimental Result (^{28}Si Growth)

◊ Growth of ^{28}Si crystal fiber is much difficult

  -- due to primarily the high impurity of the sintered disk
     from Russia

  -- smoking during heat up and formation of transparent
     particles during growth

^{28}Si growth [100] seed. Note of sharp bend
$\sim 18°$, due to inclusions. (white transparent Xtals)

^{28}Si [111] growth

2X

40 ^{28}Si crystal vacuum grown

28S (111) growth → white inclusions

128χ   28s; with inclusion
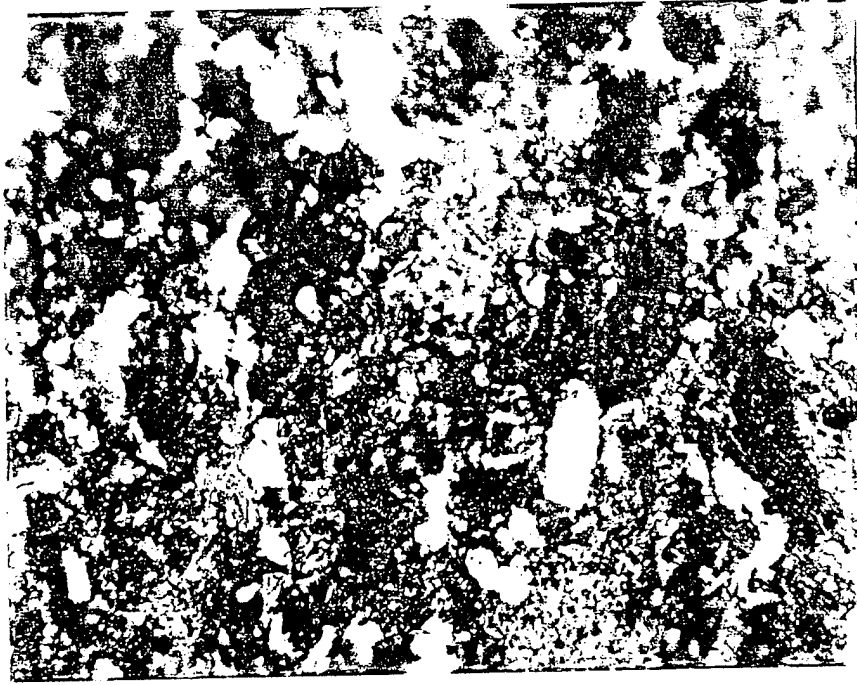
128χ   28s; feed material

§ Growth of 28Si by Melt Freeze Technique:

◊ Despite the success of LHPG, the material is simply too small for practical measurement

-- needs minimum 4 x 7 mm surface area

◊ Decided to use melt freeze technique to form small droplet single crystals of Si.

◊ Fundamental problem as compared to Ge

    -- high melting point of 1420°C vs. 937.4°C
    -- difficult to build a low cost furnace with minimum impurity and isotope contaminations
    -- difficult to find a compatible crucible

◊ Converting a conventional vertical induction heated Cz furnace with alumina bubble insulation and dense alumina tube.

    -- System first flushed with N_2 gas overnight and then N_2 with 5% H_2 gas several hours at high temperatures

    -- PBN crucibles (for MBE use) were used to melt the silicon charge.

    -- However, there still has a slight reaction and the charge sticks to the crucible. Brown color coatings on BN crucible.

◊ All three types of Si were melted to form droplets.

    -- 28Si charge is far more difficult to melt than regular Si

    -- Droplets surface is shinning but polycrystalline

§ Material Characterization:

◊ **Electric Resistivity and Hall Effect Measurement**

-- Two slabs were cut from the droplets and double side polished with finished thickness of 1.23 mm

-- Hall effect is based on van der Pauw method at both 77 and 300°K. The resistivity is in the range of 10^{-3} ohm-cm corresponding to a carrier concentration of $6 \times 10^{19}/cm^3$
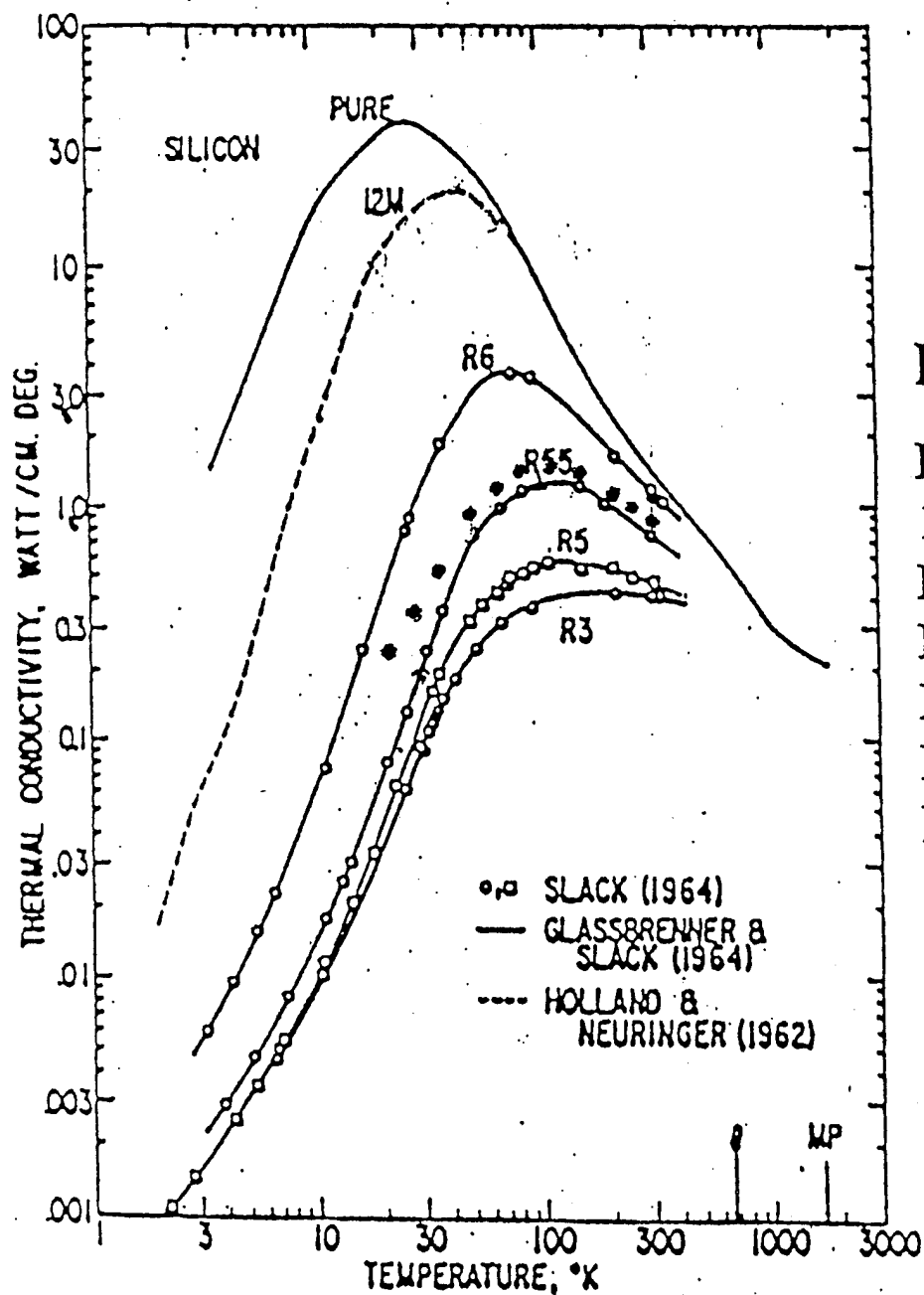
◊ **Thermal Conductivity Measurement**

-- Sample cut to $1.23 \times 1.48 \times 6.9$ mm^3 bars

-- Steady-state, longitudinal heat flow method

-- K in the range of 1 W/cm°K which fall right into the range of Slak's plot for Si resistivity of 10^{-3}.
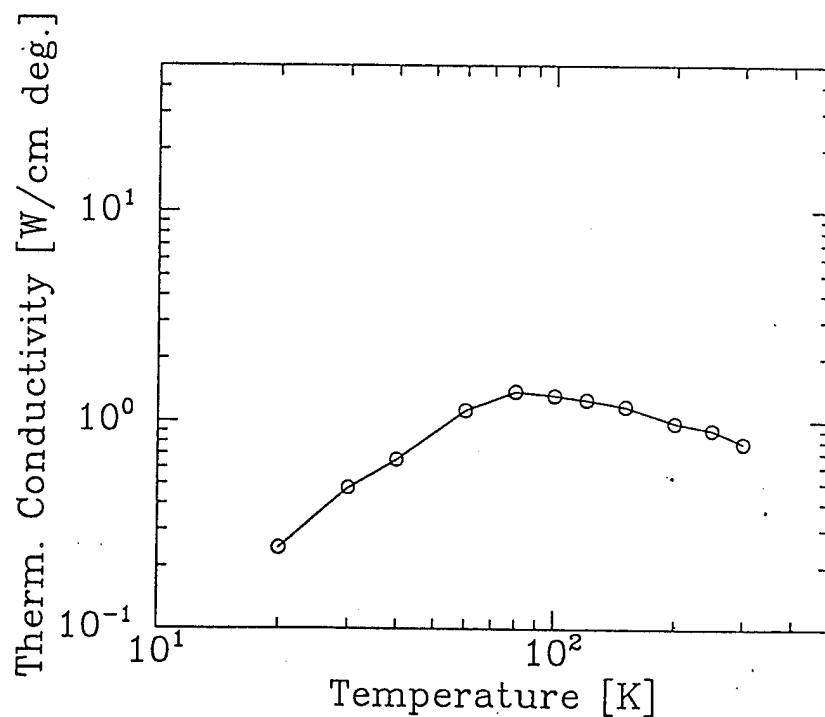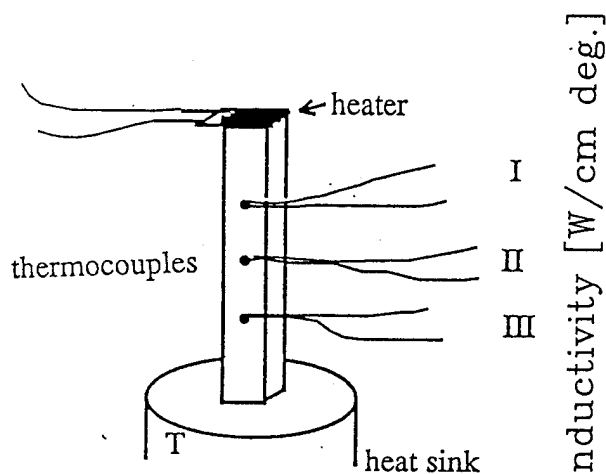
Resistivity (Ω . cm)

Pure : 200
12M : ?
R6   : $2.8 * 10^{-3}$
R55 : $6.7 * 10^{-4}$
R5   : $4.5 * 10^{-4}$
R3   : $2.6 * 10^{-4}$
Exp. dots : 5K

§ Discussion:

◊ Our result is somewhat discouraging due to high impurity contamination of the starting materials. We are unable to isolate the isotopic effect.

◊ Our result is consistent with the published doped Si result indicating our measurement technique is adequate.

◊ A recent report by Itoh et al at Lawrence Berkeley Lab. on the growth of ^{70}Ge and ^{74}Ge single crystals by vertical Bridgman techniques.

- -- Large quantity of materials used (> 100 gms)
- -- Horizontal zone purification using graphite boat
- -- Quartz tube used for atmosphere control
- -- After 25 zone passes → carrier concentration down from >>10^{17}/cm^3 to 10^{12}/cm^3.
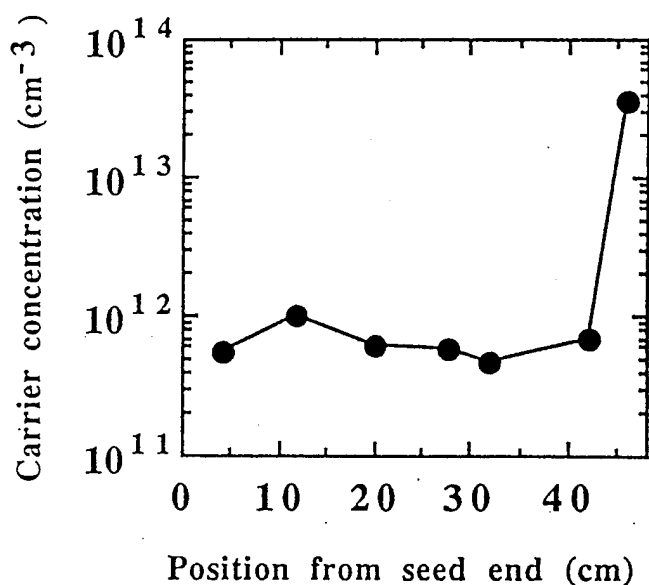- -- No report on thermal conductivity measurement

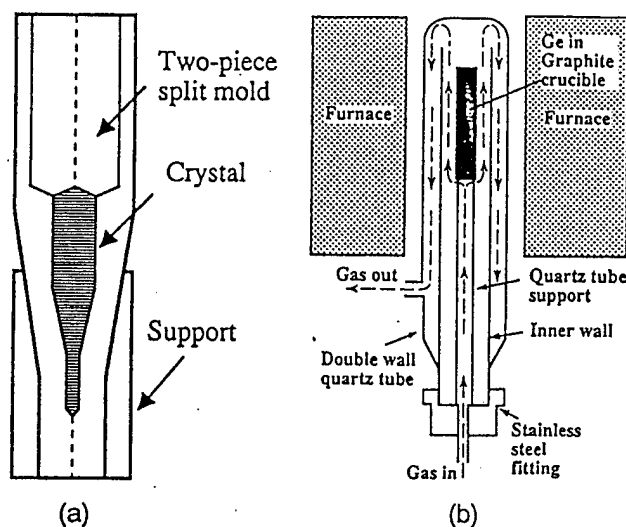FIG. 1. Net carrier concentration profile of the ^{70}Ge polycrystalline bar after 25 zone-refining passes.

FIG. 2. (a) Cross section schematic of the split graphite crucible. (b) Schematic of the seedless vertical Bridgman Ge crystal growth system.

§ Summary and Future Plans:

◊ Despite the power limitation, we succeeded the growth of Si single crystal fiber using LHPG.

◊ High impurity concentration of ^{28}Si prevent us to isolate the isotopical effect

◊ Despite the success of Ge isotope crystal growth, the technique can not be applied directly to Si due to high melting temp.

◊ A proposed method to grow high purity ^{28}Si single crystals

  -- production of high purity ^{28}Si powder
  -- isostatic sintering to solid block
  -- zone refining via LHPG
  -- single crystal growth via LHPG

◊ Need a high power (>100W) CO_2 laser